

DESCRIPTION

EPOXY RESIN COMPOSITION AND SEMICONDUCTOR DEVICE

TECHNICAL FIELD

The present invention relates to an epoxy resin composition for encapsulating of semiconductors which is suitable for the so-called area mounting type semiconductor devices formed by mounting semiconductor elements on one side of a printed circuit board or a metallic lead frame and encapsulating with a resin substantially only the side on which the semiconductor elements are mounted, and to a semiconductor device manufactured using the resin composition.

BACKGROUND ART

With the recent market trend of miniaturization, weight-saving and enhancement of performance of electronic devices, high integration of semiconductor elements has progressed year by year and surface mounting of semiconductor devices has been accelerated. Under the circumstances, area mounting type semiconductor devices have been developed afresh, and semiconductor devices of conventional structures are being switched over to the area mounting type semiconductor devices.

Representatives of the area mounting type semiconductor devices are BGA (ball grid array) and CSP (chip scale package) which pursues further miniaturization, and these have been developed for meeting the demand for

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increase of pins and speed up which has reached nearly the limit in conventional surface mounting type semiconductor devices such as QFP and SOP. The structure of the area mounting type semiconductor devices is such that semiconductor elements are mounted on one side of rigid circuit boards such as BT resin/copper foil circuit board (bismaleimide·triazine resin/glass cloth substrate) or flexible circuit boards such as polyimide resin film/copper foil circuit board and only the semiconductor elements-mounted side, namely, only the one side of the boards is molded and encapsulated with an epoxy resin composition or the like. Furthermore, the structure is characterized in that solder balls are arranged in plane on the other side of the boards for bonding to a circuit board on which a semiconductor device is mounted. Moreover, as the boards on which semiconductor elements are mounted, structures using metallic substrates such as lead frames have also been developed in addition to the above organic substrates.

The structure of these area mounting type semiconductor devices has the form of one side encapsulating, that is, only the side of the board on which semiconductor elements are mounted is encapsulated with an epoxy resin composition and the side on which solder balls are formed is not encapsulated. In the case of metallic substrates such as lead frame, an encapsulating resin layer of about several ten μms is sometimes present also on the solder ball-formed side, while an encapsulating resin layer of

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about several hundred μms to several millimeters is formed on the semiconductor element-mounted side, and, as a result, this is substantially one side encapsulating. Therefore, in these semiconductor devices, warping is apt to occur just after molding because of differences in thermal expansion heat shrinkage between the organic substrate or the metal substrate and the cured product of the epoxy resin composition or because of cure shrinkage at the time of molding and curing of the epoxy resin composition. Furthermore, when these semiconductor devices are bonded onto circuit boards with solder, this is conducted through a heating step at 200°C or higher, during which warping of the semiconductor devices occurs and many solder balls are not in flat state and are apart from the circuit boards to cause deterioration in reliability of electrical bonding.

In order to decrease warping in semiconductor devices in which substantially only one side of the board is encapsulated with an epoxy resin composition, there are two important methods, one of which comprises making thermal expansion coefficient of the substrate and that of cured epoxy resin composition close to each other, and the other of which comprises reducing cure shrinkage of the cured product of epoxy resin composition.

Resins having a high glass transition temperature (hereinafter referred to as " T_g ") such as BT resin and polyimide resin are widely used for organic substrates, and these have a T_g higher than about 170°C which is the molding

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temperature of an epoxy resin composition. Therefore, during the cooling step of from the molding temperature to room temperature, shrinkage occurs only in the area of $\alpha 1$ of the organic substrate. Accordingly, it is considered that if the cured product of epoxy resin composition also has a high Tg and the same $\alpha 1$ as that of the organic substrate and, besides, is zero in the cure shrinkage, the warping is nearly zero. Thus, there has been already proposed a method of raising the Tg by combination of a polyfunctional epoxy resin and a polyfunctional phenolic resin and meeting the $\alpha 1$ by adjusting the amount of inorganic filler to be added.

Moreover, in the case of carrying out solder bonding by solder treatments such as infrared reflowing, vapor phase soldering and solder dipping, water present in the semiconductor device due to absorption from the cured product of an epoxy resin composition and the organic substrate is abruptly vaporized at a high temperature to produce a stress, which causes cracking of the semiconductor device or separation at the interface between the semiconductor element-mounted side of the organic substrate and the cured product of the epoxy resin composition. Thus, it is demanded to diminish the stress and the absorption of moisture of the epoxy resin composition and, in addition, to allow the epoxy resin composition to have adhesion to the organic substrate.

Moreover, because of difference between thermal expansion coefficient of the organic substrate and that of

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the cured product of epoxy resin composition, separation at the interface of organic substrate/cured product of epoxy resin composition or package cracking occurs also in a heat cycle test which is a representative reliability test.

5 In the conventional surface mounting type semiconductor devices such as QFP and SOP, a crystalline epoxy resin such as biphenyl epoxy resin and a phenolic resin having a flexible skeleton are used in combination for inhibition of cracking or separation at the interface
10 between the materials at the time of mounting with solder and the amount of an inorganic filler is increased to decrease Tg and the absorption of moisture. However, these methods cannot still solve the problem of warping in one side-encapsulated semiconductor devices.

15 DISCLOSURE OF INVENTION

 The present invention provides an epoxy resin composition which causes little warping after molding or solder treatment in area mounting type semiconductor devices and is excellent in reliability of solder treatment
20 or the like because it is especially excellent in adhesion to organic substrates, and a semiconductor device manufactured using the epoxy resin composition.

 The present invention relates to an epoxy resin composition for encapsulating of semiconductors which
25 comprises (A) an epoxy resin, (B) a phenolic resin, (C) a curing accelerator and (D) an inorganic filler as main components, characterized in that properties of a cured

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product formed by heating and curing the epoxy resin composition satisfy expressions, $a \geq 10^R$ ($R=10 \times (b+c)-1$), $300 \leq a \leq 20000$ and $0.15 \leq b+c \leq 0.50$ in which a denotes a flexural modulus (N/mm^2) at molding temperature, b denotes a cure shrinkage (%) and c denotes a heat shrinkage (%) of from molding temperature to room temperature, and, particularly, to the above epoxy resin composition wherein the cured product has a water absorption rate of not more than 0.2% by weight after the cured product is treated for 168 hours in an environment of 85°C and 60% in relative humidity and the epoxy resin and/or the phenolic resin have/has a naphthalene skeleton, and to a semiconductor device manufactured by encapsulating semiconductor elements with said epoxy resin composition.

15 BRIEF DESCRIPTION OF DRAWING

FIG. 1 is a graph which shows relations of flexural modulus, cure shrinkage and heat shrinkage of the cured products of the epoxy resin compositions in examples and comparative examples.

20 DETAILED DESCRIPTION OF INVENTION

In order to reduce warping in semiconductor devices in which substantially only one side of the substrate is encapsulated with an epoxy resin composition, two methods have been considered to be important, namely, the one which comprises making the thermal expansion coefficient of the substrate and that of the cured product

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of the epoxy resin composition close to each other and the other which comprises reducing the cure shrinkage of the epoxy resin composition. That is, it is necessary for the reduction of warping to reduce the cure shrinkage and the heat shrinkage of from molding temperature to room temperature in an epoxy resin composition comprising as main components an epoxy resin, a phenolic resin, a curing accelerator and an inorganic filler.

However, reduction of the warping is still insufficient only by carrying out reduction of the cure shrinkage and the heat shrinkage from molding temperature to room temperature, and as a result of the intensive research conducted by the inventor, it has been found that the flexural modulus of the cured product obtained by heating and curing the epoxy resin composition comprising the components (A)-(D) as main components which is measured at the molding temperature, greatly affects the warping. That is, it has been found that when the flexural modulus at molding temperature is low, warping is large, and that when the flexural modulus is high, warping is small. It has further been found that all of the flexural modulus at molding temperature, the cure shrinkage and the heat shrinkage of from the molding temperature to room temperature affect the warping in combination.

Thus, it has been found that when flexural modulus (N/mm^2) at molding temperature of the cured product is expressed by a, cure shrinkage (%) of the cured product is expressed by b and heat shrinkage (%) of from molding

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temperature to room temperature is expressed by c , if these properties satisfy the expressions, $a \geq 10^R$ ($R=10 \times (b+c)-1$), $300 \leq a \leq 20000$ and $0.15 \leq b+c \leq 0.50$, the warping decreases and the soldering crack resistance is improved in the semiconductor devices in which substantially only one side of the substrate is encapsulated with the epoxy resin composition.

The molding temperature in the present invention means a temperature of a mold when the epoxy resin composition is cured by heating and is usually in the range of 160-190°C, but it is not limited to this temperature range.

The value "a" is measured in accordance with JIS K 6911.

The value "b+c" is obtained in the following manner. A cured product in the form of a disk of 100 mm in diameter and 3 mm in thickness is molded using a transfer molding machine under the conditions of a mold temperature of 175°C, an injection pressure of 70 kg/cm² and a curing time of 90 seconds, and inner diameter of the mold cavity at 175°C and outer diameter of the disk cured product at room temperature (25°C) are measured. The value "b+c" is calculated from the formula, $[(\text{inner diameter of the mold cavity at } 175^\circ\text{C}) - (\text{outer diameter of the disk cured product at } 25^\circ\text{C})] / (\text{inner diameter of the mold cavity at } 175^\circ\text{C}) \times 100$.

The cured product used for evaluation is one which has not been subjected to post-curing treatment.

In the relations of a , b and c , when a is not less than 10^R (where $R=10 \times (b+c)-1$), warping decreases and

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this is preferred, and when a is less than 10^R , warping increases and this is not preferred. Furthermore, when a is less than 300, the cured product becomes soft at curing and molding to cause deterioration of releasability from the mold, namely moldability, and when a exceeds 20000, fluidity is insufficient and moldability is deteriorated. Moreover, when $b+c$ is less than 0.15, cure shrinkage at molding and curing is small and releasability from the mold is insufficient to cause deterioration of moldability, and when $b+c$ exceeds 0.50, heat shrinkage is large and due to the increase of internal stress, soldering crack resistance is lowered.

It is preferred that the cured product obtained by heating and curing the epoxy resin composition of the present invention has a moisture absorption rate of not more than 0.20% by weight after the cured product is treated for 168 hours in an environment of 85°C and 60% in relative humidity. If the moisture absorption rate exceeds 0.20% by weight, in the case of carrying out the solder bonding by solder treatment, water which is present in a semiconductor device due to the absorption from the cured product of the epoxy resin composition and the organic substrate, is abruptly vaporized at high temperatures to produce a stress, which causes cracking in the semiconductor device or separation at the interface between the semiconductor element-mounted side of the organic substrate and the cured product of the epoxy resin composition, resulting in deterioration of soldering crack resistance.

The cured product used for measurement of the moisture absorption rate is one which is removed from the mold and then post-cured at 175°C for 2 hours.

The epoxy resins used in the present invention include all of monomers, oligomers and polymers having an epoxy group, for example, triphenolmethane type epoxy resins, biphenyl type epoxy resins, bisphenol type epoxy resins, stilbene type epoxy resins, o-cresol novolak type epoxy resins, epoxy resins having a naphthalene skeleton, and dicyclopentadiene type epoxy resins. These may be used each alone or in admixture. Especially, when epoxy resins having a naphthalene skeleton are used, flexural modulus at molding temperature is high, cure shrinkage and heat shrinkage of from molding temperature to room temperature are small, and moisture absorption rate is low, and, hence, these epoxy resins are preferred.

The phenolic resins used in the present invention include all of monomers, oligomers and polymers having two or more phenolic hydroxyl groups capable of forming a crosslinked structure upon curing reaction with the above epoxy resins. Examples thereof are phenolic novolak resins, cresol novolak resins, phenolic aralkyl resins such as p-xylylene-modified phenolic resins and m-xylylene-p-xylylene-modified phenolic resins, resins having a naphthalene skeleton, terpene-modified phenolic resins, and dicyclopentadiene-modified phenolic resins. These may be used each alone or in admixture. Especially, when the resins having a naphthalene skeleton are used, flexural

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modulus at molding temperature is high, cure shrinkage and heat shrinkage of from molding temperature to room temperature are small, and moisture absorption rate is low, and these resins are preferred.

5 The curing accelerators used in the present invention are those which can act as catalysts for cross-linking reaction of the epoxy resin with the phenolic resin. Examples of them are 1,8-diazabicyclo(5,4,0)-undecene-7, amine compounds such as tributylamine, organic
10 phosphorus compounds such as triphenylphosphine, tetraphenylphosphonium · tetraphenyl borate, and imidazole compounds such as 2-methylimidazole. The curing accelerators are not limited to these examples. These may be used each alone or in admixture.

15 The inorganic fillers used in the present invention have no special limitation and those generally used for encapsulating materials can be used. Examples thereof are fused silica, crystalline silica, secondary aggregation silica, alumina, titanium white, aluminum
20 hydroxide, talc, clay, and glass fibers. The fused silica is especially preferred. The fused silica may be either in crushed or spherical form, but it is more preferred to use mainly spherical silica for increasing amount thereof to be added and inhibiting increase of melt viscosity of the
25 epoxy resin composition. In order to further increase the amount of spherical silica to be added, it is desirable to carry out adjustment so that particle size distribution of spherical silica becomes broader.

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With regard to the proportions of components (A) to (D) in the epoxy resin composition of the present invention, the proportion of a phenolic resin (B) is 20-300 parts by weight, the proportion of a curing accelerator (C) is 0.1-30 parts by weight, and the proportion of an inorganic filler (D) is 200-2000 parts by weight on the basis of 100 parts by weight of an epoxy resin (A). When the proportion of a phenolic resin (B) is less than 20 parts by weight, curing is insufficient, and when said proportion exceeds 300 parts by weight, the problem that uncured material remains is caused. When the proportion of a curing accelerator (C) is less than 0.1 part by weight, it takes a long time until curing is completed, and when said proportion exceeds 30 parts by weight, curing proceeds rapidly and satisfactory cured product cannot be obtained. When the proportion of an inorganic filler (D) is less than 200 parts by weight, soldering crack resistance is inferior, and when said proportion exceeds 2000 parts by weight, fluidity of the resin composition becomes bad to give insufficient moldability.

The epoxy resin composition of the present invention may optionally contain, in addition to the components (A)-(D), various additives, for example, flame retardants such as brominated epoxy resin, antimony oxide and phosphorus compounds, inorganic ion exchangers, coupling agents, coloring agents such as carbon black, releasing agents such as natural wax, synthetic wax, higher fatty acids and metallic salts thereof and paraffin, low

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stress components such as silicone and rubber, and antioxidants.

The epoxy resin composition of the present invention is obtained by mixing the components (A)-(D) and other additives by a mixer, then heating and kneading the mixture by a kneader such as a heating kneader, a hot roll and an extruder, and cooling and grinding the kneaded product.

For producing semiconductor devices by encapsulating electronic parts such as semiconductor elements with the epoxy resin composition of the present invention, the composition can be cured and molded by conventional molding methods such as transfer molding, compression molding and injection molding.

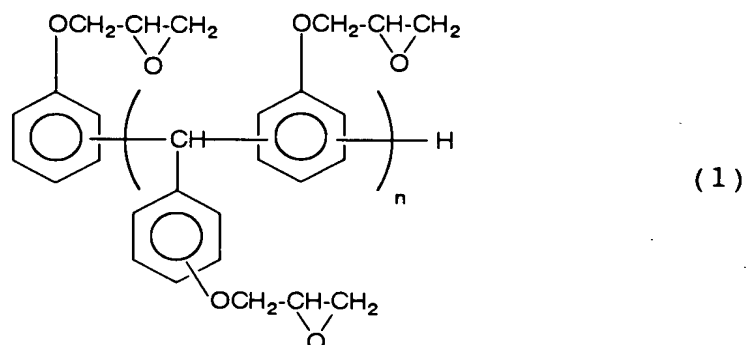
BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be explained specifically by the following examples. The proportions of various components are expressed by part by weight.

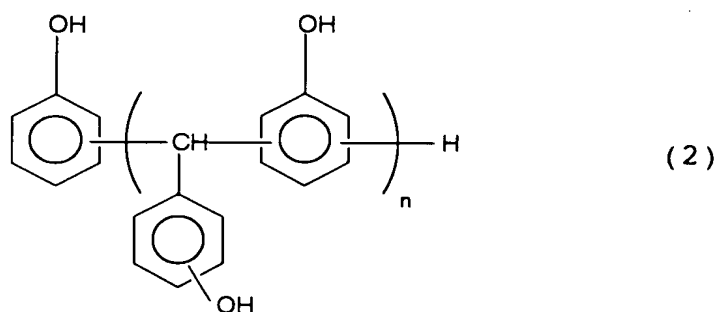
Example 1

10.2 Parts by weight of an epoxy resin represented by the following formula (1) (Epikote 1032H manufactured by Yuka Shell Epoxy Co., Ltd.; softening point: 60°C, epoxy equivalent: 170):

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5.8 parts by weight of a phenolic resin represented by the following formula (2) (MEH7500 manufactured by Meiwa Kasei Co., Ltd.; softening point: 105°C, hydroxyl equivalent: 97):



0.15 part by weight of triphenylphosphine, 83.25 parts by weight of spherical fused silica (average particle diameter: 15 μ m), 0.3 part by weight of carnauba wax and 0.3 part by weight of carbon black were mixed by a mixer, then the mixture was kneaded using a twin roll having surface temperatures of 90°C and 45°C for 5 minutes, and the kneaded product was cooled and then ground to obtain an epoxy resin composition. The resulting epoxy resin composition was evaluated by the following methods. The results are shown in Table 1.

Evaluation methods:

Spiral flow: Measurement was conducted using a mold for measurement of spiral flow in accordance with EMMI-1-66 under the conditions of a mold temperature of 175°C, an injection pressure of 70 kg/cm² and a curing time of 2 minutes.

Curability: Measurement was conducted using Shore "D" durometer under the conditions of a mold temperature of 175°C, an injection pressure of 70 kg/cm² and a curing time of 90 seconds.

Flexural modulus "a" at molding temperature: Measurement was conducted in accordance with JIS K 6911 as mentioned above. A cured product was molded using a transfer molding machine under the conditions of a mold temperature of 175°C, an injection pressure of 70 kg/cm² and a curing time of 90 seconds, and the flexural modulus was measured at 175°C. The unit was N/mm².

"b+c": As mentioned above, a cured product in the form of a disk of 100 mm in diameter and 3 mm in thickness was molded using a transfer molding machine under the conditions of a mold temperature of 175°C, an injection pressure of 70 kg/cm² and a curing time of 90 seconds, and inner diameter of the mold cavity at 175°C and outer diameter of the disk cured product at room temperature (25°C) were measured. The value "b+c" was calculated from the formula, $[(\text{inner diameter of the mold cavity at } 175^{\circ}\text{C}) - (\text{outer diameter of the disk cured product at } 25^{\circ}\text{C})] / (\text{inner diameter of the mold cavity at } 175^{\circ}\text{C}) \times 100$. The unit

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was %.

Moisture absorption rate: A disk of 50 mm in diameter and 3 mm in thickness was molded using a transfer molding machine under the conditions of a mold temperature of 175°C, an injection pressure of 70 kg/cm² and a curing time of 90 seconds, and post-cured at 175°C for 2 hours. The cured product was further treated for 168 hours in an environment of 85°C and 60% in relative humidity, and change of weight was measured. The unit was % by weight.

10 Warping amount of package: A 225pBGA (BT resin substrate of 0.36 mm in thickness; chip size: 12 mm × 12 mm × 0.35 mm thick; package size: 24 mm × 24 mm; thickness of encapsulating resin: 1.17 mm) was molded using a transfer molding machine under the conditions of a mold temperature of 175°C, an injection pressure of 70 kg/cm² and a curing time of 90 seconds, and post-cured at 175°C for 2 hours. The cured product was cooled to room temperature, and, thereafter, displacement in the height direction was measured using a surface roughness meter in diagonal direction from the gate of the package. The largest value of displacement was taken as amount of warping. The unit was μm.

25 Soldering crack resistance: The above 225pBGA was molded, and post-cured at 175°C for 2 hours to obtain ten samples. These were treated for 168 hours in an environment of 60°C and 60% in relative humidity or in an environment of 85°C and 60% in relative humidity, and, then, treated by IR reflowing (240°C) for 10 seconds. The samples

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were observed by an ultrasonic defectoscope to examine the presence of internal cracks and various interfacial separations. When the number of defective packages was n , this was expressed by $n/10$.

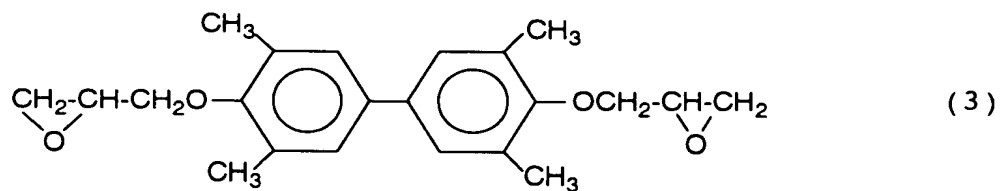
- 5 Releasability: Releasability from the mold at the time of molding of the above 225pBGA was examined. The product which was not smoothly removable from the mold was judged to be bad.

Examples 2-6 and Comparative Examples 1-6

- 10 Components were mixed in accordance with Tables 1 and 2, and epoxy resin compositions were prepared in the same manner as in Example 1 and these were evaluated in the same manner as in Example 1. The results are shown in Tables 1 and 2. Structures and properties of the epoxy
15 resins and phenolic resins used in the examples and the comparative examples are shown below.

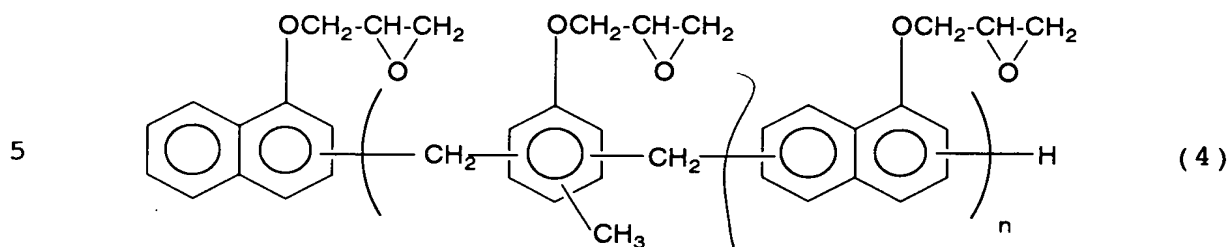
- Epoxy resin comprising a main component represented by the following formula (3) (YX-4000H manufactured by Yuka Shell Epoxy Co., Ltd.; melting point: 105°C,
20 epoxy equivalent: 195):

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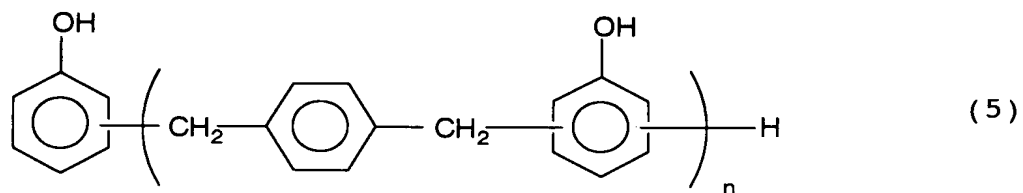


Epoxy resin represented by the following formula

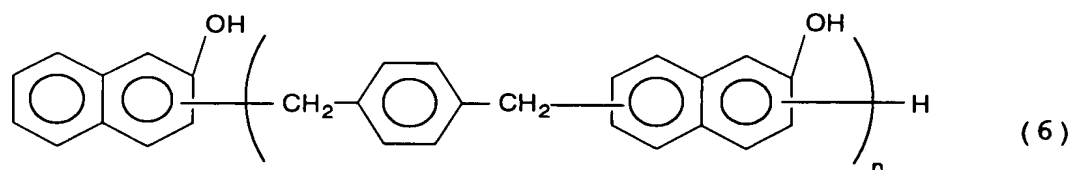
(4) (NC7000 manufactured by Nippon Kayaku Co., Ltd.;
softening point: 90°C, epoxy equivalent: 225):



Phenolic resin represented by the following formula (5) (softening point: 83°C, hydroxyl equivalent: 175):



10 Phenolic resin represented by the following
formula (6) (softening point: 80°C, hydroxyl equivalent:
200):



Phenolic novolak resin (softening point: 80°C,
hydroxyl equivalent: 105).

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Table 1

	Example					
	1	2	3	4	5	6
Epoxy resin of formula (1)	10.2	10.2				7.6
Epoxy resin of formula (3)			4.2	5.9		
Epoxy resin of formula (4)					6.4	
Phenolic resin of formula (2)	5.8	5.8				4.4
Phenolic resin of formula (5)			3.8			
Phenolic resin of formula (6)				6.1	5.6	
Spherical fused silica	83.25	83.30	91.25	87.20	87.30	87.30
Triphenylphosphine	0.15	0.10	0.15	0.20	0.10	0.10
Carbon black	0.3	0.3	0.3	0.3	0.3	0.3
Carnauba wax	0.3	0.3	0.3	0.3	0.3	0.3
Spiral flow (cm)	100	100	80	70	80	70
Curability	95	95	90	95	95	95
Flexural modulus a (N/mm ²)	14000	8000	1500	600	1500	10000
b + c (%)	0.28	0.42	0.40	0.28	0.20	0.20
Moisture absorption rate (wt%)	0.26	0.27	0.10	0.10	0.09	0.22
Releasability	Good	Good	Good	Good	Good	Good
Warping amount of package (μ m)	50	80	80	30	20	30
Soldering crack resistance (60°C)	0/10	0/10	0/10	0/10	0/10	0/10
Soldering crack resistance (85°C)	10/10	10/10	0/10	0/10	0/10	8/10

Table 2

	Comparative Example					
	1	2	3	4	5	6
Epoxy resin of formula (1)				4.9	7.6	12.7
Epoxy resin of formula (3)	10.7	6.3	5.2			
Phenolic resin of formula (2)	5.3				4.4	7.3
Phenolic resin of formula (5)		5.7				
Phenolic novolak resin			2.8	3.1		
Spherical fused silica	83.25	87.20	91.35	91.35	87.15	79.10
Triphenylphosphine	0.15	0.20	0.05	0.05	0.25	0.30
Carbon black	0.3	0.3	0.3	0.3	0.3	0.3
Carnauba wax	0.3	0.3	0.3	0.3	0.3	0.3
Spiral flow (cm)	100	80	70	70	20	140
Curability	95	85	50	85	95	100
Flexural modulus a (N/mm ²)	400	1000	200	1600	24000	17000
b + c (%)	0.38	0.45	0.16	0.13	0.20	0.52
Moisture absorption rate (wt%)	0.16	0.11	0.08	0.15	0.26	0.33
Releasability	Good	Good	Bad	Bad	Unfilled	Good
Warping amount of package (μ m)	110	120	40	30	Unfilled	130
Soldering crack resistance (60°C)	0/10	0/10	0/10	0/10	Unfilled	10/10
Soldering crack resistance (85°C)	2/10	0/10	0/10	5/10	Unfilled	10/10

As clear from the above Table 1, the area mounting type semiconductor devices obtained using the epoxy resin composition of the present invention are less in warping after molding or soldering treatment and excellent
5 in soldering crack resistance.

INDUSTRIAL APPLICABILITY

The epoxy resin composition of the present invention can be applied to encapsulating of various semiconductor devices and is especially suitable for BGA
10 (ball grid array) and CSP (chip scale package). The semiconductor devices obtained by encapsulating with the resin composition of the present invention can be used for computers, liquid crystal display devices, portable telephones and the like.

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